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The connection between the heat storage capability of PCM as a material property and their performance in real scale applications

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Abstract

Using phase change materials (PCM) for Thermal Energy Storage, the most important material property is their heat storage capability, usually given as $h(T)$. Ideally, $h(T)$ changes suddenly at a single temperature. However, many PCM change phase in a temperature range and show hysteresis. In addition, experience shows that even measurements with the same device on the same material can give different results when the heating rate, the amount of sample mass or the equipment device are varied. The question thus arises how to deal with different $h(T)$ results when trying to predict the performance of a real scale application. This paper identifies the main origins of these effects and gives strategies for dealing with them.

Keywords: *Phase Change Material (PCM); material property; latent heat; heat capacity; enthalpy; hysteresis*

1 Introduction

The accurate knowledge of material properties to predict the performance of an application is a common problem in R&D. Using Phase Change Materials (PCM) for Thermal Energy Storage (TES), the most important material property is the heat storage capability, usually given as the enthalpy h as a function of temperature T (Fig. 1).

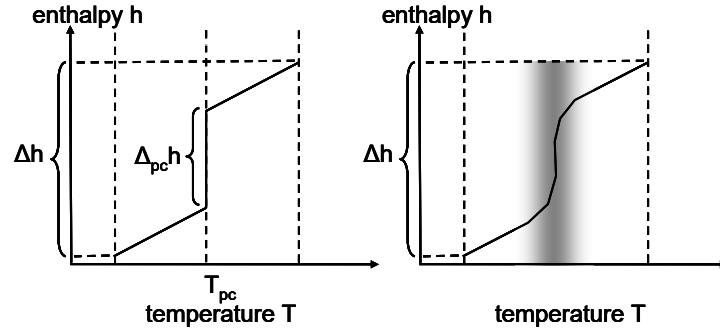


Fig. 1 Enthalpy h as a function of temperature T for the case of a phase change temperature and a phase change temperature range

In an idealized case, the enthalpy changes suddenly at a phase change temperature. The heat stored is then called latent heat, while heat stored with a temperature change is called sensible heat. The latter is described by the heat capacity c (thus, the term heat storage capability is used here to refer to heat storage in general). However, many PCM change phase in a temperature range and this must be taken into account when applying such PCM in a real application.

In addition, heating and cooling processes often show different thermal behaviour, called hysteresis (Fig. 2). This includes subcooling, which means that for the material to change to the lower temperature phase (in a solid-liquid phase change the solid phase), a certain temperature lower than the phase change temperature has to be reached to start the phase change. At this temperature, the nucleation temperature T_{nuc} , a small nucleus of the lower temperature phase forms.

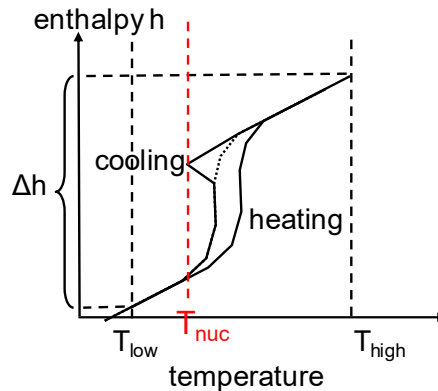


Fig. 2 Enthalpy h as a function of temperature T for the case of a phase change temperature range, here with hysteresis including subcooling

Subcooling is very common when using the phase change between solid and liquid. In addition to these effects, experience shows that even measurements with the same device on the same material can give different results for $h(T)$ [Lázaro et al. 2013]. The question thus arises how to

deal with different $h(T)$ results when trying to predict the performance of an application. The topic of this paper is to review and investigate these effects and to give strategies for dealing with them.

2 Basics

The performance of real scale applications is commonly derived from the behaviour of the materials they are composed of, which are described by their material properties. A material (or substance) is what things are made of. As such, a material is composed of many atoms in a defined consistency, in a homogeneous or heterogeneous way. Objects consist of a single or several materials, in a certain amount, size, shape, etc. A material property is a property that is characteristic for the material, and therefore depends on the material by its composition, but not on amount, size, and shape. Examples are the density of a material, its thermal conductivity, melting point, etc. Material properties in general depend on boundary conditions like temperature, pressure, etc.

Material properties are generally determined by a measurement on a sample in an idealized situation. To be able to use material properties to predict the performance of an application some general conditions have to be met.

2.1 Representative sample – choosing a suitable sample

The material has to be well defined to be able to say that characterization and application refer to the same material (representative sample). The selection and preparation of a suitable sample is thus crucial. Special care has to be taken when a material is heterogeneous, such that a sample is large enough to have the consistency of the material to be characterized.

2.2 Repeatable result – getting the same result reliably again

For a measured property to be a material property, that means to be characteristic for the behaviour of a material and thereby to allow a prediction of the performance of an application, it is necessary that the material behaves the same under the same conditions, meaning the measured property has a repeatable result. Repeatability then refers to the closeness of the agreement between the results of successive measurements of the same measurand (particular quantity subject to measurement) carried out under the same conditions of measurement [JCGM 2008].

For example, the heat capacity of liquid water at 20°C and ambient pressure is always the same; it is a material property. The same holds for the phase change enthalpy between solid and liquid at ambient pressure. The heat of combustion of a material is the same for the same material under the same conditions, and is thus also a material property (but for repeated measurements new samples have to be used). The history of the material therefore plays a crucial role. The crystallinity in a glass transition depends on the cooling rate, and not only on the boundary conditions like temperature and pressure. It can thus only be seen as a material property if the history of the material, here the cooling rate, is included in the definition of the material. Regarding PCM, the most crucial case is its cycling stability, referring to the PCMs heat storage capability during repeated phase change cycles.

2.3 Reproducible result – transferring the material property to the application

The conditions of the sample when determining the material property are in general different from the conditions in the application. To be able to transfer the result of the material property to the application the result must be reproducible, that means the same, or at least similar enough. Reproducibility of results of measurements refers to the closeness of the agreement between the results of measurements of the same measurand carried out under changed conditions of measurement [JCGM 2008].

Therefore, unless well known, it is better to scan a range of conditions and not a single value. Specifically, the amount of the material is always different between material characterization and application, and the boundary conditions are different at least in most cases.

When using PCM, the most important one is the temperature, as PCM are selected for thermal energy storage specifically because of their high heat storage capability in a narrow temperature range. Therefore, $h(T)$ has to be determined in a temperature range covering the phase change with sufficient resolution in the temperature (resolution = density of data points in a parameter range) as well as with sufficient accuracy in the temperature (accuracy = closeness of the agreement between the result of a measurement and a true value of the measurand, quantified by the uncertainty [JCGM 2008]) (Fig. 3).

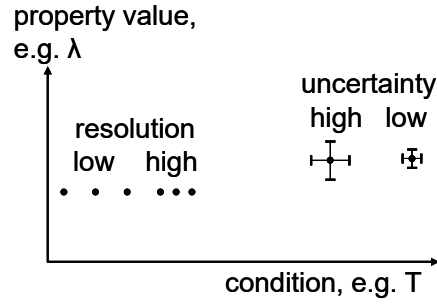


Fig. 3 Meaning of resolution and accuracy (quantified by the uncertainty)

Nevertheless, additional effects could be due to different pressures, surfaces, etc. Further on, it is common measurement practice to investigate several samples, and measure each sample several times to check reproducibility and repeatability of the results.

3 Observed effects in material property determination

The connection between the heat storage capability of PCM as a material property and their performance in real scale applications is now reviewed and investigated.

The first point mentioned above, the representative sample, is a matter of selecting a sample and a measurement device with sufficient sample size. The second and third points, regarding repeatable and reproducible (transferable) results, are now discussed in detail, each connected with an example. Before, however, it is necessary to assure that the result of a measurement is correct at all, a problem arising due to the specific properties of PCM.

The most obvious point when doing material characterization is that the material property must be determined correctly. Material properties in general depend on boundary conditions, like pressure p , temperature T , etc. When using PCM, the most important one is the temperature, as PCM are selected for TES specifically because of their strong change in enthalpy in a narrow temperature range. For calculations or simulations of real scale applications, experience in R&D shows that $h(T)$ needs to be known at least with a temperature resolution of 1°C , and an accuracy better than $\pm 1^\circ\text{C}$ in temperature and $\pm 10\%$ for the enthalpy change [Günther et al. 2009]. When doing material characterization in a calorimeter, the necessary heat flux to scan a temperature range leads to a temperature gradient in the sample; it depends on the chosen sample size and geometry, the chosen heating respectively cooling rate, and the materials thermal conductivity and heat storage capability. Due to the temperature gradient, the measured thermal effect is due to a temperature range, but in evaluation for $h(T)$ it is associated to a single temperature. This effect, which is especially pronounced when measuring PCM, leads to an

artificial hysteresis and has been studied intensively in the past decade. Early works by the ZAE Bayern [Günther et al. 2009, Castellón et al. 2008] and the FhG-ISE for quality control of PCM within the framework of the RAL quality association PCM (www.pcm-ral.de) resulted in the recommendation to vary the heating and cooling rate to identify heating and cooling rates where this effect is minimized such that temperature equilibrium and thus a single temperature within the sample is reached [Vidi et al. 2014] (or at least almost reached). In recent years, this has been investigated in a larger group within the IEA Task 42 / Annex 24 and Task 42 / Annex 29. Fig. 4 shows results of a DSC measurement of octadecane applying different heating and cooling rates; the results show a significant effect of the heating and cooling rate, with large hysteresis when applying high heating and cooling rate. As the change in enthalpy from solid to liquid remains the same, the change in heating and cooling rate had no effect on the crystallinity (in many substances, high cooling rates can lead to a partly amorphous structure which has a much lower phase change enthalpy).

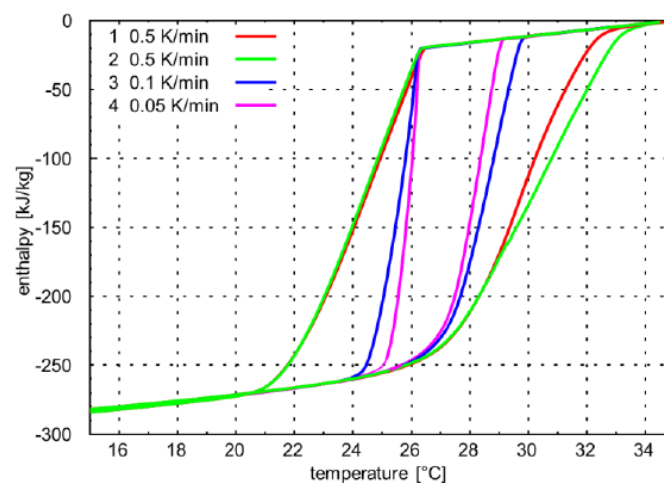


Fig. 4 Results of a DSC measurement on octadecane applying different heating and cooling rates [Gschwander et al. 2015].

Fig. 5 shows results from a larger group using different DSC instruments and all low heating and cooling rates [Gschwander et al. 2015]. The results show that using low heating and cooling rates the results agree well, meaning that the hysteresis observed before was to a large extent artificially caused by the chosen heating and cooling rate, and not a property of the material.

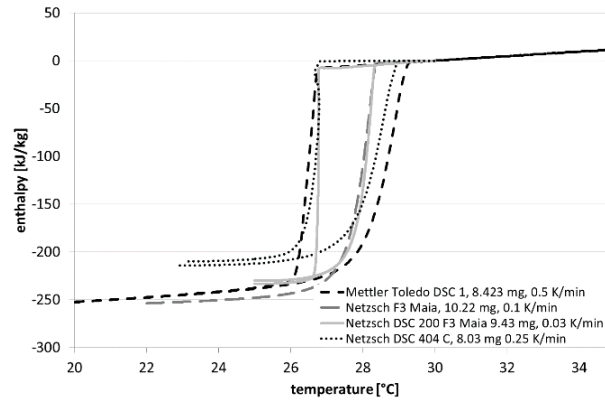


Fig. 5 Results for octadecane from a larger group using different DSC instruments and all applying small heating and cooling rates [Gschwander et al. 2015]. The larger offset is from an evaluation of the peak integral only.

The data of practically all PCM measured on heating and on cooling in the past indicate large hysteresis. As it was common to measure with high heating and cooling rates, the observed hysteresis is probably artificial in many, if not in most cases. When measuring close to thermal equilibrium by applying a low heating and cooling rate, it is possible to eliminate artificial effects due to the measurement and arrive at values that are characteristic for the material. The good agreement of the results in Fig. 5, using different DSC instruments, also shows that today $h(T)$ can be determined with different DSC to an accuracy better than $\pm 10\%$ and $\pm 1^\circ\text{C}$ for the temperature [Gschwander et al. 2015]. With this knowledge on how to measure $h(T)$ correctly, that means with temperature equilibrium in the sample, other effects of the material can be studied. The following are just a few examples showing some of the observed effects.

As a first example it is interesting to look at chemically very similar materials. The data from [Gschwander et al. 2015] for octadecane show only about 1K difference between the heating and from cooling enthalpy curves; the material thus shows very little hysteresis in $h(T)$, if at all (the observed 1 K could still be at least partly due to a measurement effect). In contrast, polyethylene (PE) shows significant hysteresis of typically more than 10 K between heating and cooling curves, even if the heating and cooling rates are low like 0.5 K/min using DSC as is shown in Fig. 6; PE thus has significant hysteresis in $h(T)$. To obtain the results of HDPE shown in Fig. 6, the experiments were performed in 40 μL aluminum closed crucibles under 80ml·min⁻¹ N₂ flow between 100-150 °C.

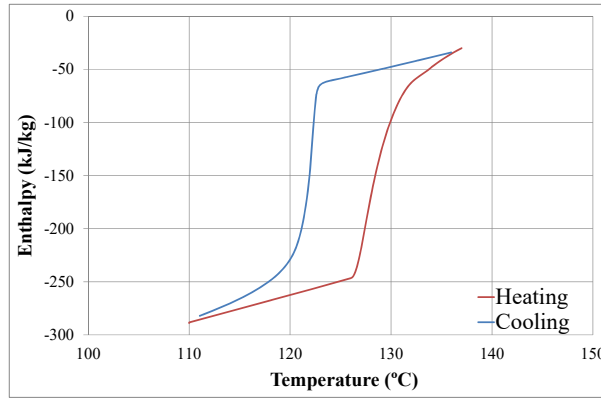


Fig. 6 DSC results obtained for HDPE, 0.5 K/min heating and cooling curves

Polyethylene also shows another interesting effect: the total enthalpy change upon phase change depends on the sample history. Müller et al. 2012 report a significantly different phase change enthalpy after a sample of UHMW-PE was melted the first time. Polyethylene in the solid phase consists of a crystalline and an amorphous fraction. Different heating or cooling rates could lead to a different fraction of the crystalline phase, and thus to a different phase change enthalpy. In addition, the fraction of crystalline phase also affects the density; this is already well known from the terms high density polyethylene (HDPE) and low density polyethylene (LDPE); the reason here is often the molecular structure of the polyethylene used. A change in the phase change enthalpy thus could also be due to a different pressure, e.g. when PE is produced. The repeatability of $h(T)$ thus depends on the sample history, and a careful selection of a representative sample is necessary.

Another effect caused by the crystalline phase is observed in some sugar alcohols, such as erythritol and d-mannitol: different solid phases exist, called polymorphism, and depending on which solid phase results upon cooling the enthalpy difference on cooling varies [Barreneche et al. 2013]. Repeatability is thus a serious problem. Moreover, Solé et al. 2014 proved that temperature range analysis affects the results leading to different polymorphic phases thus different phase change temperatures. Therefore, it should be studied for each PCM under conditions closer to real application and controlled except when equilibrium values are required. Then, Gschwander et al. [Gschwander et al. 2015] measurement procedure must be followed.

This effect can be seen in Fig. 7, where two different temperature ranges are applied to the same PCM, in this case d-mannitol, under the same conditions (sample size of around 20 mg and heating/cooling rate at 1 K/min).

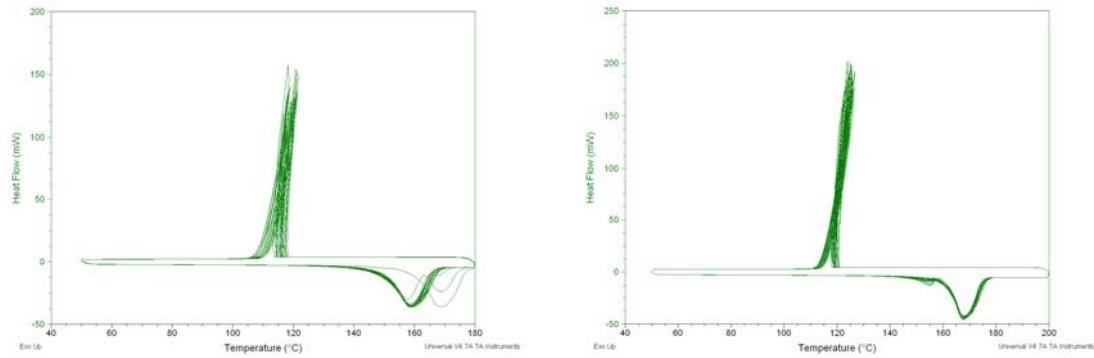


Fig. 7 d-mannitol tested at 1 K/min under different temperature ranges, left: 50-180 °C and right: 50-200 °C, leading to different polymorphic phases with different melting ranges.

Also in this publication, what it is observed and experimentally tested to affect the thermal cycling stability of most sugar alcohols is oxygen presence. Without oxygen in contact, the results after several melting and freezing cycles are repeatable.

Subcooling is present to some degree in many PCM. For water, it is well known that temperatures down to -40°C can be reached in DSC measurements where the sample size is in the order of tens of μl . In T-history experiments, with sample sizes in the order of 10 ml, temperatures between -10°C and -5°C are reached. In larger amounts of about 1 l, nucleation occurs at about -3°C to -2°C . A systematic study for different PCM was done by [Rathgeber et al. 2015]. The observed subcooling in measurements for materials characterization thus depends on the sample size. But even more, the amount of material can be different in real scale applications. It is thus advisable to scan a sample size range, or to measure the performance in a real scale size in order to include the option to measure small sizes if the variation shows no difference. Nucleation can also be initiated by impurities, such that a change in composition or a change in the container walls between material characterization and real scale application can lead to different performance. For this reason, the RAL quality association PCM suggests to give $h(T)$ for heating and for cooling without the effect of subcooling (as indicated by the dotted line in Fig. 2), and to give the nucleation temperature as a separate value for conditions comparable to an application.

While in most cases the amount of material in the application is larger than in material characterization, there are exceptions. For example paraffins are used for PCM emulsions, where the amount of PCM in a single, isolated droplet is much smaller than the sample size in a typical DSC measurement. This behavior has been studied by [Huang et al. 2010] and also showed additional, size dependant effects: hexadecane emulsions showed significant subcooling, while non-emulsified (bulk) hexadecane does not.

A very important topic in this context is phase separation, when referring to cycling stability. It is known to depend on the size of the “sample”. To fight separation it is therefore common to reduce the effective size of the “sample” by dividing it into many small parts by gelling and thickening. Therefore, the performance of a gelled or thickened PCM cannot be derived from a measurement of the pure PCM.

4 From observed effects to predictions for an application

How to do a correct measurement of $h(T)$ has been investigated thoroughly and can be considered a more or less solved problem today at least when using DSC [Gschwander et al. 2015]. However, how to select a representative sample, and how to find out which of the observed effects are repeatable, reproducible and transferable under which conditions is not that well studied and frequently unclear. After discussing the different observed effects and their origins, the question how to deal with different $h(T)$ results when trying to predict the performance of an application has to be answered. There are several strategies for dealing with them.

As a basic information on repeatability and reproducibility of $h(T)$ results it is in general necessary to investigate several samples, and measure each several times. As the result is affected also by the sample history, the sample can be cooled with different cooling rates before doing a measurement (see effects in PE). To check additionally if a sample is representative different sources (manufacturers), purities, etc. can be investigated.

To check for reproducibility as well as transferability it is advisable to identify the conditions that affect the result, e.g. sample size, pressure, temperature (as in the case of d-mannitol), container walls, etc.; if one of them has a significant effect this effect must be investigated and the magnitude of the effect determined (see subcooling [Rathgeber et al. 2015]).

Connected with this is to determine the necessary $h(T)$ and acceptable subcooling in an application and to analyze the needed accuracy of the data (sensitivity of the prediction to the material property). In this context an error analysis of the determined material property is also advisable.

Last, but not least, calculations or simulations of the performance of an application are usually based on a single $h(T)$ data set. To deal with hysteresis or irreproducible behavior it is always advisable to use best case and worst case $h(T)$ data in different scenarios.

5 Summary and outlook

Using phase change materials (PCM) for Thermal Energy Storage, the most important material property is their heat storage capability, usually given as $h(T)$. Ideally, $h(T)$ changes suddenly at a single temperature. However, many PCM change phase in a temperature range and show hysteresis. In addition, experience shows that even measurements with the same device on the same material can give different results. The question thus arises how to deal with different $h(T)$ results when trying to predict the performance of a real scale application.

In this paper, the crucial points regarding this question have been identified: choosing a representative sample, checking if a result is repeatable, and finally if it is reproducible and at which conditions a result from material characterization can be used to predict the performance in an application. For PCM, main origins for getting different results have been identified and discussed, and finally strategies for dealing with them were given.

Previous investigations (Gschwander et al. 2015 and Lázaro et al. 2013) looked at effects originating from the h - T determination by DSC, meaning the calorimeter and its use. For this, materials without complex behaviour were investigated. The results are in good agreement when using low heating and cooling rates, meaning that the hysteresis observed before was caused, to a large extent, by the chosen heating and cooling rate, and disregarding the possibility of being a material property. In this paper the effects shown by materials with a more complex behaviour as well as the relation to different conditions between measurement and application are highlighted.

For most PCM a detailed investigation of the different effects is still missing. Materials characterization and determination of material properties thus will remain to be important topics.

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